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(54) High temperature articles

(57) A high temperature article, for example a rocket nozzle suitable for liquid-fuelled rocket motors for satellites, is formed from an alloy which is a binary or tertiary alloy from the Pt-Ir-Rh system. Such alloys exhibit a good balance between ease and reliability of manufacture, cost of alloy and high temperature strength and oxidation resistance.

Description

The present invention concerns improved high temperature articles, such as rocket nozzles.

Space vehicles, such as satellites, require many rocket motors and nozzles for positioning. These structures are usually operated at temperatures in excess of 2000°C and are required to sustain substantial structural loads. At these temperatures, oxidation of the material generally occurs resulting in a decrease in efficiency. In general, materials capable of withstanding such high temperatures with minimal oxidation, do not have the strength to withstand substantial loads. Conversely, materials capable of withstanding substantial loads at those temperatures are generally subject to considerable oxidation. Consequently, rocket motors have been operated at below optimum temperatures in order to maintain structural strength with minimal oxidation. Even so, the life of such structures was generally limited.

Attempts have been made to overcome these problems. UK patent application GB 2,020,579A proposes the use of 10% by weight rhodium/platinum alloy for use in high-velocity gas streams, but this alloy has a markedly lower ability to withstand high operating temperatures. US Patent 4,917,968 uses an iridium/rhenium bi-layer composite, formed by chemical vapour deposition (CVD) of iridium onto a molybdenum mandrel followed by deposition of rhenium and dissolution of the molybdenum. A CVD process by its nature is generally limited to the application of pure metals and therefore gives no real opportunity to use the advantages of alloying.

There remains concern, however, within the aerospace industry about the reliability of the manufacturing process and the reliability of the nozzles formed by the above process. The investment in a satellite and its launch is such that there must be complete confidence in all parts.

Consequently there remains a need in the industry for alternative rocket nozzles having reliable and acceptable manufacturing methods combined with acceptable high temperature properties. It is desirable to be able to operate the rocket motor at as high a temperature as possible, since this equates to using less fuel for a given thrust, in turn permitting one or more of an increased payload, fuel load and the ability to maintain the satellite in position for an increased life.

The present inventors have found an alloy system which can withstand the high temperatures and loads required by the various applications. These alloy systems show good oxidation resistance and have the added benefit of greater ductility which gives improved fabricability, and more predictable failure mode.

Accordingly, the present invention provides a high temperature article prepared from an alloy capable of sustaining substantial temperatures and loads wherein said alloy is a binary or tertiary alloy from the system platinum/iridium/rhodium, provided that if the alloy is a binary rhodium/platinum alloy, the rhodium content is greater than 25% and that if the alloy is a binary platinum/iridium alloy, the iridium content is greater than 30%.

Examples of suitable binary alloys are:

a) Rh/Ir in which the content of Rh is up to 60wt%, more preferably up to 40wt%;

b) Rh/Pt in which the content of Rh is from 25 to 40wt%, more preferably 25 to 30wt%;

c) Ir/Pt in which the content of Ir is 30 to 99.5wt%, preferably 30 to 40wt% or 60 to 99.5wt%.

Preferably the article is prepared from a Rh/Ir binary alloy, in which the Rh content is from 0.5 to 10wt%, for example 2.5 to 5wt%.

Preferred tertiary alloys are those represented on the attached triangular compositional diagram (Figure 1) as falling within the total hatched and cross-hatched area, and more preferred tertiary alloys are those falling within the cross-hatched area of the diagram.

The invention also encompasses modifications of the above alloys by the incorporation of a refractory metal such as rhenium or zirconium in an amount of up to 5% by wt, or the incorporation of other metal components providing that high temperature strength and oxidation resistance are not excessively adversely affected.

The invention further includes high temperature articles manufactured from the specified alloys and coated with a refractory metal or alloys thereof such as rhenium or tungsten/rhenium, for example by vacuum plasma spraying using conventional equipment, followed by hot isostatic pressing, or by a chemical or electrochemical deposition route.

Alternatively, the high temperature article may not be made completely from the above alloys, but may be a ceramic or metal article coated with one of the above alloys. Accordingly, an alternative embodiment of the present invention provides a coating for applying to a ceramic or metal, *eg* a refractory metal, substrate of a binary or tertiary alloy from the system platinum/iridium/rhodium, provided that if the alloy is a binary rhodium/platinum alloy, the rhodium content is greater than 25% and that if the alloy is a binary platinum/iridium alloy, the iridium content is greater than 30%.

The alloys specified form solid solutions and may be cast into ingots, forged, rolled, swaged, machined and/or drawn into tube, providing that robust tooling is used. For example, the alloy components may be melted in a vacuum furnace, although air furnaces may be used. Joining techniques used in platinum group metal metallurgy may be used.

Depending upon the properties of the alloy chosen, the high temperature article may be manufactured from tube

or by forming sheet into the appropriate shape, by joining different shaped cone and tube shapes, by progressively forming (rolling) a flared cone from a tube, or possibly by die casting or machining from a casting. In all cases, a final shape may be achieved by machining. Alternatively, the article may be manufactured by coating a substrate with the alloy using plasma spraying, particularly vacuum plasma spraying, followed by removal of the substrate, for example by dissolving the substrate, oxidising or machining out the substrate. The particular wall thicknesses will depend upon the particular article being formed, but may be of the order of 0.040in (approximately 1mm) or less.

The high temperature articles of the invention show a good balance of oxidation resistance, high temperature strength and relative ease of manufacture, leading to reliability combined with acceptable production costs.

Suitable articles according to the present invention include rocket nozzles, spark plug electrodes, electrodes *eg* for glass melting applications, glass melting and forming apparatus *eg* crucibles, stirrers, fibrising equipment, core pinning wire for investment casting *eg* turbine blade manufacture, and lead-outs for halogen bulbs.

Preferably the articles of the present invention are rocket nozzles, which may be used for main thrusters or subsidiary thrusters (positioning rockets), and are preferably used with liquid fuel rockets.

The present invention will now be described by way of Example only.

Experimental procedures

Ir metal and Ir-2.5%Rh and Ir-5%Rh alloys were melted and alloyed in air before electron beam melting into ingots. Each of the wire-bar ingots were then hot forged, hot swaged and hot drawn to wire. The sheet ingots were hot forged and hot rolled to size.

Oxidation Tests:

Furnace oxidation tests were performed on samples cut from sheet. Dimensional and weight measurements were performed before and after exposing these samples for 8 hours at 1450°C. This data was used to calculate oxidative weight loss per unit area per unit time for Ir, Ir-2.5%Rh and Ir-5%Rh. Results (in mg/cm^2/hr) (Table 1) clearly show that a Rh addition of only 2.5% is sufficient to more than halve the oxidation rate of Ir at 1450°C. Further improvement is achieved with an addition of 5%Rh. Microstructural analysis of cross sections through the tested samples did not reveal resolvable differences in oxide layer thickness.

Resistance heating of wire samples in flowing air was also performed to obtain comparative oxidation resistance at very high temperatures. This involved connecting a length of wire, nominally 1mm diameter and 50mm long, between the terminals of a variable electrical supply. Distance between the electrical terminals was fixed to ensure that each test was performed under similar conditions. Current flowing through each wire sample was increased slowly until the desired test temperature was achieved. Temperature was measured using an optical pyrometer focused on the hottest section of the wire. Tests were conducted at temperatures of 1650-1700°C for 5-6 hours, 2050-2100°C for 40 minutes and 2200-2250°C for 20 minutes. Weight measurements were performed before and after each test. Size (surface area) of the hot zone was not known though was probably similar for each test condition. Results (Table 1) are therefore presented in the form of weight loss per unit time in order to illustrate comparative performance of the three materials under similar extreme conditions. Tests performed at 1650-1700°C corroborate the findings from the furnace oxidation tests, clearly demonstrating a halving of the oxidation rate of Ir by alloying with 2.5%Rh. Tests performed at 2025-2100°C demonstrate that improvements, albeit smaller, in oxidation resistance can be obtained until, at 2200-2250°C, no difference in oxidation resistance was measured.

TABLE 1 -

Ir/Rh Oxidation Behaviour				
	Ir	Ir-2.5%Rh	Ir-5%Rh	units
Furnace oxidation tests				
8 hours at 1450°C	12.5	5.6	4.3	mg/cm^2/hr
Resistance heating of wire samples				
1700°C	21	10	11	mg/hr
2050-2100°C	77	56	64	mg/hr
2200-2250°C	132	132	133	mg/hr

Hardness Tests:

Vickers hardness tests were performed on polished microsections removed from sheet in the as-rolled condition and after 8 hours at 1450°C. The results are shown in Table 2.

TABLE 2 -

Hardness			
	Ir	Ir-2.5%Rh	Ir-5%Rh
As-rolled	536	530	566
After 8 hours at 1450°C	309	309	294

Sheet Tensile Data:

Tests were performed on dumbell samples using a servo-hydraulic tensometer. The test specimens were machined from as-rolled sheet using spark and wire erosion. Tests performed at strain rates of $0.016 min^{-1}$ and $15.8 min^{-1}$ at 20°C clearly demonstrated the significant increase in tensile strength and ductility that can be achieved through minor additions of Rh to Ir (Table 3). The retention of this high strength and ductility under high strain rate conditions is even more remarkable. At 1150°C very large deformation was obtained in both of the Ir/Rh alloys (Table 4).

Wire Tensile Tests:

Tensile tests were performed on as-drawn wire samples of Ir, Ir-2.5%Rh and Ir-5%Rh at room temperature. Wire diameter was nominally 1mm and strain rate was $0.01 min^{-1}$. Results (Table 5) for tensile elongation and reduction in area demonstrate significant improvement in the ductility of Ir by alloying with 5%Rh.

TABLE 3 - Ir/Rh Sheet Tensile Data at 20°C

Alloy	Strain Rate min^{-1}	Yield Strength MPa	Yield Strength psi	Yield Strength tsi	Tensile Strength MPa	Tensile Strength psi	Tensile Strength tsi	Elong %
Ir	0.016	approx 740			743	107,735	48	2.8
Average		740			743			2.8
	15.8				761	110,345	49	1.9
	"				713	103,385	46	1.7
Average					737			1.8
2.5%Rh/Ir	0.016	931			1097	159,065	71	5.3
	"	938			1088	157,760	70	4.1
Average		935			1093			4.7
	15.8				1314	190,630	85	10.5
	"				1177	170,665	76	6.8
Average					1246			8.7
5%Rh/Ir	0.016	1080			1307	189,515	85	8.5
	"	1107			1425	206,625	92	12.7
	"	1093		1/2	1395	202,276	90	12.3
		1093			1376			11.2
	15.8				1431	207,495	93	13.8
	"				1431	207,495	93	12.6
Average					1431			13.2

Strain rate = Variable; Specimens = sheet dumbell; As rolled

TABLE 4 - Ir/Rh Sheet Tensile Data at 1150°C

Alloy	Strain Rate min^{-1}	Tensile Strength MPa	psi	tsi	Elong %
Ir	0.016	315	45,675	20	17
Average		315			17
2.5%Rh/Ir	0.016	215	31,175	14	57
	"	193	27,985	12	70
Average		204			64
5%Rh/Ir	0.016	191	27,695	12	59
	"	205	29,725	13	73
	"	220	31,900	14	54
		205			62

Strain rate = 0.016min^{-1}; Specimens = sheet dumbell; As-rolled.

TABLE 5 - Ir/Rh - Wire Tensile Data

Alloy	Yield Strength MPa	Yield Strength psi	Yield Strength tsi	Tensile Strength MPa	Tensile Strength psi	Tensile Strength tsi	Elong %	R of A %	Comments
Ir	BRO712 0.89mm diameter as drawn wire								
				1869	271,005	121	13.2	13	fracture at 45 degrees
				1835	266,075	119	10	10	
				1869	271,005	121	10.3	11	broke in jaws
				1906	276,370	123	16.2	17	
				1872	271,440	121	7.8	1	broke in jaws
Average	1648	238,960	107	1870	271,179	121	11.5	10.4	
Standard dev				25			3.2	5.9	

Alloy	Yield Strength MPa	Yield Strength psi	Yield Strength tsi	Tensile Strength MPa	Tensile Strength psi	Tensile Strength tsi	Elong	R of A %..	Comments %
2.5%Rh/Ir	BRO888 1.05mm diameter, as drawn wire								
				1483	215,035	95	3.7	11	flat, 0 degree brittle type fracture
				1511	219,095	97.8	5.6	13	
				1560	226,200	101	7.1	14	
				1565	226,925	101	6.9	15	broke in jaw
				1623	235,335	105	12.2	19	
				1518	220,110	98.3	8.1	15	broke in jaws
				1560	226,200	101	7.7	14	broke in jaws
				1536	222,720	99.5	7.3	15	broke in jaws
				1527	221,415	98.9	10.9	16	broke in jaws
				1567	227,215	101	7.5	14	
Average	1363	197,635	88.3	1545	224,025	100	7.7	14.6	
Standard dev				39			2.4	2.1	

Alloy	Yield Strength			Tensile Strength			Elong	R of A	Comments
	MPa	psi	tsi	MPa	psi	tsi	%	%	
5%Rh/Ir	BR2489 1.06mm diameter as drawn wire								
				1784	258,680	116	28.1	40	Notable necking with fibrous cup-cone type fracture
				1837	266,365	119	34.9	45	broke in jaws
				1840	266,800	119	16.5	22	broke in jaws
				1764	255,780	114	26.9	35	
				1804	261,580	117	24.2	37	broke in jaws
Average	1501	217,645	97.2	1806	261,841	117	26.1	35.8	
Standard dev				33			6.7	8.6	

Claims

1. A high temperature article prepared from an alloy capable of sustaining substantial temperatures and loads wherein said alloy is a binary or tertiary alloy from the system platinum/iridium/rhodium, provided that if the alloy is a binary rhodium/platinum alloy, the rhodium content is greater than 25wt% and that if the alloy is a binary platinum/iridium alloy, the iridium content is greater than 30wt%.

2. A high temperature article according to claim 1 prepared from a binary alloy selected from rhodium/iridium in which the content of rhodium is up to 60wt%, rhodium/platinum in which the content of rhodium is from 25 to 40wt% and iridium/platinum in which the content of iridium is from 30 to 99.5wt%.

3. A high temperature article according to claim 2 in which the alloy is selected from rhodium/iridium in which the rhodium content is up to 40wt%, rhodium/platinum in which the rhodium content is 25 to 30wt% and iridium/platinum in which the content of iridium is 30 to 40wt% or 60 to 99.5wt%.

4. A high temperature article according to claim 3 prepared from a rhodium/iridium binary alloy in which the rhodium content is from 0.5 to 10wt%.

5. A high temperature article according to claim 1, formed from a tertiary alloy of composition represented by the hatched and cross-hatched area of the compositional diagram of Figure 1.

6. A high temperature article according to claim 4, formed from a tertiary alloy of composition represented by the cross-hatched area of the compositional diagram of Figure 1.

7. A high temperature article according to any one of the preceding claims, wherein the alloy contains up to 5wt% of a refractory metal.

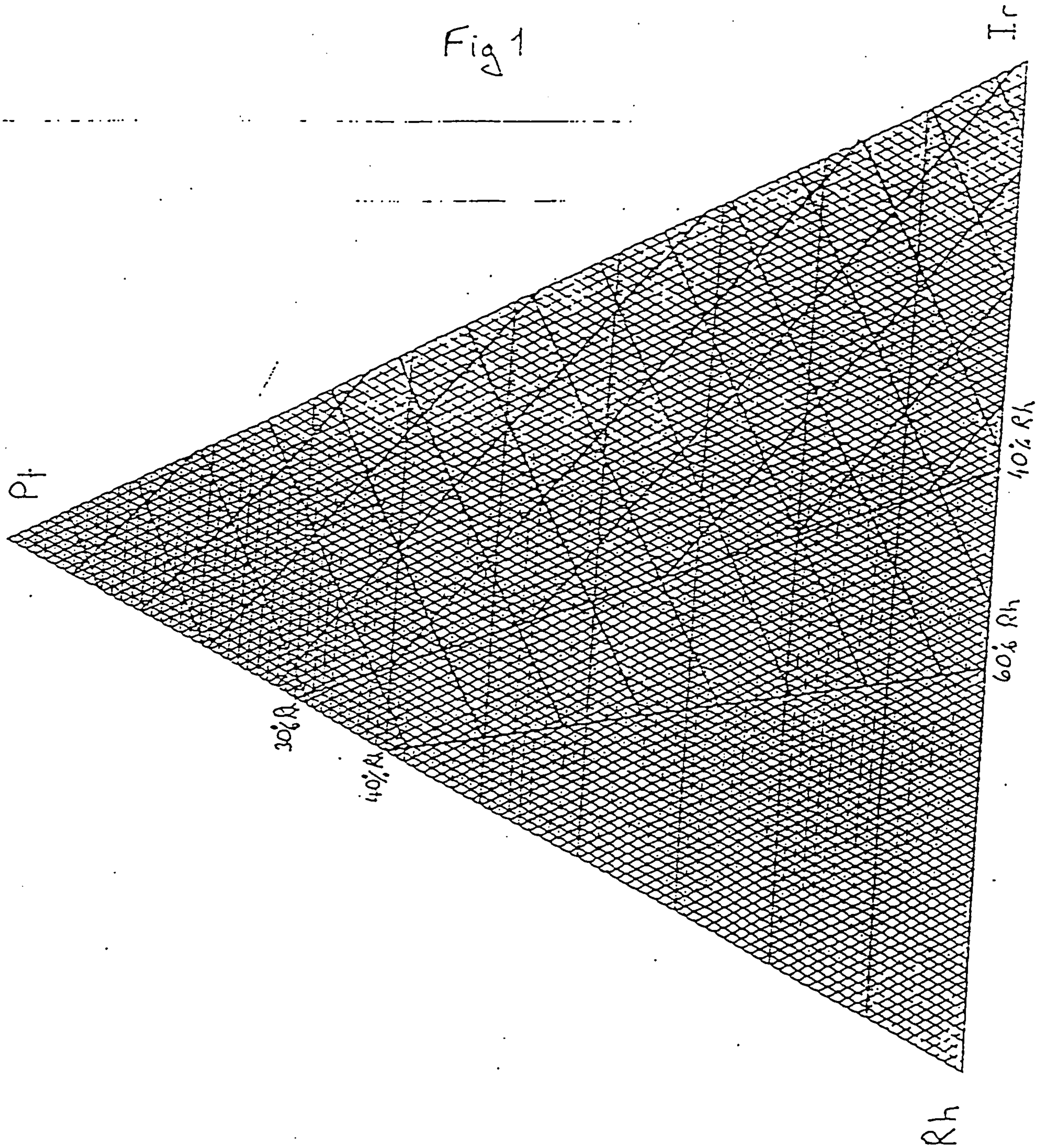
8. A high temperature article according to any one of the preceding claims, wherein the article is coated with one or more coatings of a refractory metal or alloy thereof.

9. A high temperature article according to any one of the preceding claims, wherein the article is a rocket nozzle, a spark plug electrode, an electrode, a glass melting or forming apparatus, a core pinning wire for inventment casting or a lead-out for halogen bulbs.

10. A liquid-fuelled rocket motor suitable for use with satellites or other space vehicles, comprising a rocket nozzle according to claim 9.

11. A coating for applying to a ceramic or metal substrate of a binary or tertiary alloy from the system platinum/iridium/rhodium, provided that if the alloy is a binary rhodium/platinum alloy, the rhodium content is greater than 25% and that if the alloy is a binary platinum/iridium alloy, the iridium content is greater than 30%.

Fig 1



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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 6116

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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X	T.B. MASSALSKI 'BINARY ALLOY PHASE DIAGRAMS' 1986, AMERICAN SOCIETY FOR METALS, OHIO, US *PAGES 1423, 1427, 1429, 1901 AND 1905*	1-4	
X	US-A-4 285 784 (FLINN DAVID R ET AL) 25 August 1981 * claim 1; table 2 *	1-3,7,11	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 December 1995	Gregg, N

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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X	FR-A-2 492 806 (OWENS CORNING FIBERGLASS CORP) 30 April 1982 * claim 1; example 1 *	1-3,7,9,11	
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